NEW IRON OXIDE CATALYST REDUCTION ACTIVITIES
WITH HYDROGEN SULFIDE AND HYDROGEN

H. Hattori, F.A. Jones, T. Ogawa, C.L. Knudson,
L.J. Radonovich and V.I. Stenberg

University of North Dakota Energy Research Center
and the Department of Chemistry
University of North Dakota, Grand Forks, ND 58202

INTRODUCTION

Various types of catalysts have been used for coal liquefaction. Among these catalysts, molybdenum and iron catalysts are most frequently used and they are usually combined with other metal oxides. Molybdenum catalysts, in the form of $Co/Mo/Al_2O_3$ wherein this notation represents some form of the metal oxides and the last species is the support, have been used in the H-Coal process. In others, iron catalysts have been used in the form of red mud which is mixed with elemental sulfur. The activity of iron catalysts has generally been regarded as low when compared with that of molydenum catalysts. However, iron oxide catalysts became highly active for the conversion of coal-related model compounds when used in the presence of H_2S and H_2. For coal liquefaction in the absence of a heterogeneous catalysts, the use of a mixture of H_2S and H_2 instead of H_2 resulted in an increase in conversion.[1] Because of the interaction of H_2S with Fe_2O_3[2] and the fact that iron is presently the lowest cost transition metal, iron was selected as the basis metal for a new set of heterogeneous catalysts specifically designed for coal liquefaction using the H_2S-H_2 reducing gas medium.

EXPERIMENTAL

A series of 26 iron oxide catalysts were designed and synthesized. The supported iron catalysts prepared are listed in Table 1. The selection of the supports were based on the following objectives.
1. To clarify the effect of SiO_2 surface area, SiO_2 supports for catalysts 1, 2, and 3 were prepared at different pH's from a Na-free SiO_2 source.
2. To examine the effect caused by use of a different starting material to prepare SiO_2, catalysts 4, 5, and 6 were prepared from sodium metasilicate at different pH's and can be compared to catalysts 1-3.

287

3. To examine the effect of the precipitating reagent, catalysts 7 and 8 were prepared from $Si(OC_2H_5)_4$ with H_2SO_4 or NaOH, respectively. Catalysts 7 and 8 results are to be compared with those of catalysts 1 and 3.

4. To examine the effect of basic supports, metal oxides with basic properties were used for the supports of catalysts 9, 10, 11, 12, 13 and 14.

5. To examine the effect of the sulfate ion on the TiO_2 support, it was prepared in the presence of sulfate ions and the resulting catalyst 15 is to be compared with catalyst 14.

6. To examine the effect of additives to Fe/SiO_2, small amounts of Mo, W, Co, and Ni oxides were added (catalysts 16, 17, 18, and 19) to the Fe_2O_3 on the surface of the catalyst.

7. To examine the effect of the sulfate and nitrate anions on the deposition of the iron layer, catalysts 20 and 21 were prepared.

8. To examine the effect of acidic sites on the Fe/SiO_2 catalyst, sodium- and potassium-poisoned catalysts were prepared (catalysts 22 and 23).

9. To examine the effects of the commercial TiO_2 and SiO_2 supports, catalysts 20 and 24 were prepared to be compared to catalysts 1 and 14, respectively.

10. To examine the effect of activated carbon which possesses an extremely high surface area as the Fe_2O_3 supports, catalyst 26 was prepared to be compared to catalyst 20 (SiO_2) and 24 (TiO_2).

11. To examine the effect of a simple admixture of Fe_2O_3 and SiO_2, catalyst 28 was prepared to be compared with catalyst 20.

12. To enable comparison to a known commerical hydrogenation catalyst, $Co/Mo/Al_2O_3$ (catalyst 29) was included as a part of the series.

The catalysts were subjected to two reactions: hydrocracking of diphenylmethane to toluene and benzene, a model compound for the Ar-C bond cleavage of the coal structure, and hydrocracking of diphenyl ether to phenol and benzene, a model compound for the Ar-O bond cleavage of the coal structure. The reaction conditions for these reactions are summarized in Table 2.

RESULTS AND DISCUSSION

The design of the iron oxide catalysts was based on the following experimental findings.

1. For the hydrocracking of diphenylmethane, the effect of H_2S addition was augmented with iron oxide catalysts.[3]

2. The promotional effect of the H_2S addition on the catalytic activity varied with the preparative method for iron catalyst.[3] Among Fe catalysts supported on SiO_2, ZrO_2, and TiO_2, the Fe/SiO_2 showed the highest activity for the hydrocracking of diphenylmethane.

3. The Fe/TiO_2 catalyst was active not only for hydrocracking of diphenylmethane but also for hydrocracking of diphenyl ether.[3]

Besides these findings, it has been generally observed that the catalytic behavior of active components vary with the types of supports.

The time dependence of the diphenylmethane conversion is depicted in Figure 1. The value of 20 minutes reaction time was selected for the tubing bomb tests in order to differentiate catalyst effects.
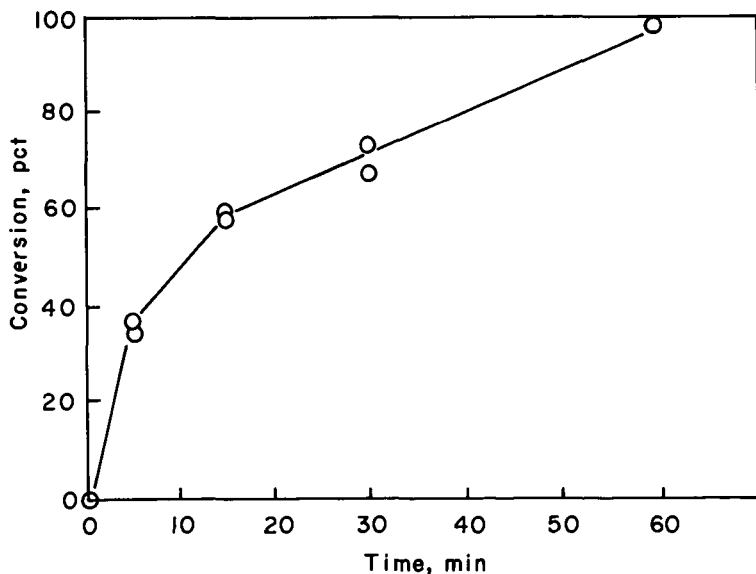

Fig. 1. Time dependence of conversion for hydrocracking of diphenylmethane. Catalyst, Fe_2O_3/SiO_2 (catalyst 20); catalyst/reactant, 50 mg/500 mg; reaction temperature, 425°C; pressure at room temperature, H_2 700 psi, H_2S 100 psi; and reactor, 12-ml capacity.
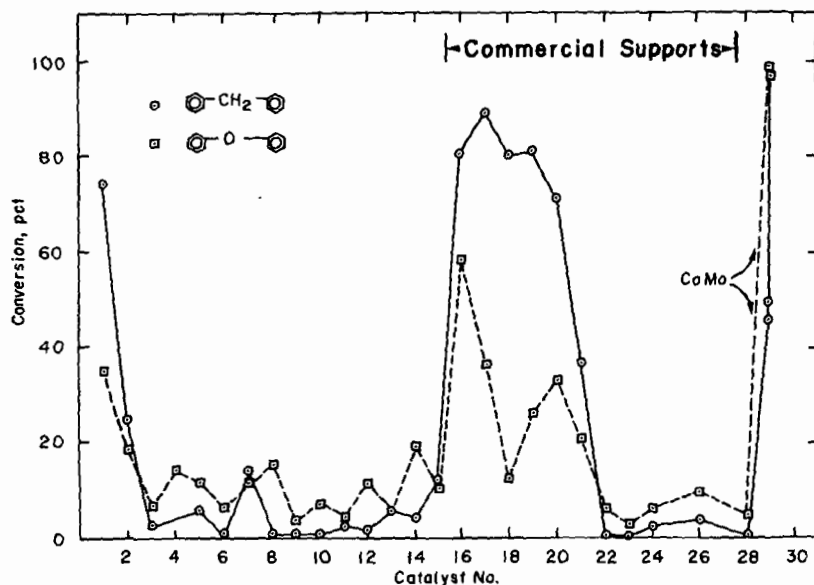
Fig. 2. Conversion of diphenylmethane (—) and diphenylether
(---) with various catalysts.

The results of the catalytic reactions are given in Figure 2. For hydrocracking of diphenylmethane, the activities vary with different supports. This indicates that an interaction of Fe_2O_3 with the support occurred. The activity increased with an increase in surface area of support (catalysts 1, 2, and 3). Enhanced catalytic activity was observed by addition of Mo (no. 16), W (no. 17), Co (no. 18), and Ni (no. 19) oxides to the surface Fe_2O_3 as compared to Fe/SiO_2 (no. 20). The introduction of sodium or potassium to Fe/SiO_2 eliminated the catalytic activity (nos. 22 and 23 vs. no. 20). Similar phenomena were observed for catalysts 5, 6, and 8, which possibly contain sodium on the support. The sulfate ion had a negative influence on catalytic activity, cf. catalyst 5 with 2.

290

For the hydrocracking of diphenyl ether, the catalyst containing Mo and Fe (catalyst 16) was twice as active as the iron oxide catalyst. However, hydrogenated products such as methylcyclopentane and cyclohexane were produced in larger quantities with catalyst 16 than with 20. The Fe/SiO$_2$ catalyst activity increased with increased surface area of the support (catalysts 1-3), and was poisoned by sodium and potassium ions, cf. catalysts 22 and 23 with 20. The presence of the sulfate ion again retarded the Fe/SiO$_2$ activity, cf. nos. 15 to 14 and 20 to 21, as it did with diphenylmethane.

In general the catalysts required the presence of hydrogen sulfide[4] and the commercially supplied sample of silica with its high surface area worked very well. The pH of the silica preparation method proved to be crucial to generating high surface area silica. The catalysts in which the iron oxides were deposited on silica exceeded or equaled the activity of a simple admixture of iron oxide and silica (catalyst 28). The iron oxide catalysts were the better than the commercial hydrogenation-hydrocracking catalyst Co/Mo/Al$_2$O$_3$ for the hydrocracking of diphenylmethane (e.g., catalyst 20 vs. 29) but the latter exhibited both hydrocracking and hydrogenation ability. However, the Co/Mo/Al$_2$O$_3$ was more active in the conversion of diphenyl ether.

ACKNOWLEDGEMENT

REFERENCES

1. (a) Sondreal, E.A.; Wilson, W.G., and Stenberg, V.I., Mechanisms Leading to Process Improvements in Lignite Liquefaction Using CO and H$_2$S, _Fuel_, 1982, _61_, 926. (b) Baldwin, R.M. and Viciguerra, _Fuel_, 1982, _62_, 498. (c) Abdel-Baset, M. and Ratcliffe, C.T., _Preprints Amer. Chem. Soc. Div. Fuel Chem._, 1979, _25_, 1. (d) Satterfield, C.M. and Model, M., _U.S. NTIS, P.B. Rept._, 1975, 248101.

2. (a) Ogawa, T.; Stenberg, V.I., and Montano, P.A., _Fuel_, 1984, in press. (b) Stenberg, V.I.; Tanabe, K.; Ogawa, T.; Sweeny, P. and Hei, R., Iron-Based Catalysts, H$_2$S and Liquefaction, Preprints, Fuel Division, American Chemical Society, 1983, National Meeting of the American Chemical Society, Washington, D.C.

3. Stenberg, V.I.; Ogawa, T.; Willson, W.G. and Miller, D., Hydrocracking of Dephenylmethane, _Fuel_, 1982, _62_, 1487.

4. (a) Stenberg, V.I.; Srinivas, V.R.; Sweeny, P.; Baltisberger, R.J. and Woolsey, N.F., Dealkylation of N,N-dimethylaniline with Sulphur and Hydrogen Sulphide, Fuel, 1983, 62, 913. (b) Baker, G.G.; Willson, W.G.; Farnum, B.W., and Stenberg, V.I., Homogeneous Catalysis of Lignite Liquefaction with Hydrogen Sulfide, 1983 Spring National AlChE Meeting, Utilizing Texas Lignite, Session 16D, Fuels and Petrochemicals Division, March 27-31, Houston, Texas.

Table 2. Reaction conditions

Reaction	Temperature (°/C)	Ratio of reactant/catalyst by wt.	Pressure (psi cold charge) H_2S	H_2	Reaction time (1 min)
Hydrocracking of diphenylmethane	425	10/1	100	700	20
Hydrocracking of diphenyl ether	425	10/1	100	1400	60

Table 1. List of catalysts prepared

No.	Catalyst Composition (wt. ratio)	Source of Fe_2O_3	Surface area (M^2/g)	Starting Material	Support Precipitation Reagent	pH
1	Fe/SiO$_2$ (1/9)	Fe(NO$_3$)$_3$	579	Si(OC$_2$H$_5$)$_4$	HNO$_3$	1
2	Fe/SiO$_2$ (1/9)	Fe(NO$_3$)$_3$	382	Si(OC$_2$H$_5$)$_4$	HNO$_3$	5
3	Fe/SiO$_2$ (1/9)	Fe(NO$_3$)$_3$	28	Si(OC$_2$H$_5$)$_4$	NH$_4$OH	11
4	Fe/SiO$_2$ (1/9)	Fe(NO$_3$)$_3$	578	Na$_2$SiO$_3$	H$_2$SO$_4$	1
5	Fe/SiO$_2$ (1/9)	Fe(NO$_3$)$_3$	349	Na$_2$SiO$_3$	H$_2$SO$_4$	5
6	Fe/SiO$_2$ (1/9)	Fe(NO$_3$)$_3$	318	Na$_2$SiO$_3$	H$_2$SO$_4$	11
7	Fe/SiO$_2$ (1/9)	Fe(NO$_3$)$_3$	568	Si(OC$_2$H$_5$)$_4$	H$_2$SO$_4$	1
8	Fe/SiO$_2$ (1/9)	Fe(NO$_3$)$_3$	39	Si(OC$_2$H$_5$)$_4$	NaOH	11
9	Fe/CaO (1/9)	Fe(NO$_3$)$_3$	1	Ca(OH)$_2$	—(calcined at 500°C)—	
10	Fe/La$_2$O$_3$ (1/9)	Fe(NO$_3$)$_3$	11	La(NO$_3$)$_3$	NH$_4$OH	9
11	Fe/ZrO$_2$ (1/9)	Fe(NO$_3$)$_3$	74	ZrOCl$_2$	NH$_4$OH	9
12	Fe/ZnO (1/9)	Fe(NO$_3$)$_3$	5	Zn(NO$_3$)$_2$	NH$_4$OH	9
13	Fe/SnO$_2$ (1/9)	Fe(NO$_3$)$_3$	28	SnCl$_2$	NH$_4$OH	9
14	Fe/TiO$_2$ (1/9)	Fe(NO$_3$)$_3$	41	TiCl$_4$	NH$_4$OH	9
15	Fe/TiO$_2$ (1/9)	Fe(NO$_3$)$_3$	56	TiCl$_4$ + (NH$_4$)$_2$SO$_4$	NH$_4$OH	9

Table 1. (continued)

No.	Catalyst Composition (wt. ratio)	Source of Fe_2O_3	Surface area (M^2/g)	Support Starting Material	Precipitation Reagent	pH
16	$Mo/Fe/SiO_2$ (1/9/90)	$Fe(NO_3)_3$ + $(NH_4)_6Mo_7O_{24}$	477	Commercial. Fisher Sci. Co.		
17	$W/Fe/SiO_2$ (1/9/90)	$Fe(NO_3)_3$ + $(NH_4)_{12}W_{12}O_{42}$	496	Catalog No. S-156. 14-20 mesh Lot No. 744571		
18	$CoFe/SiO_2$ (1/9/90)	$Fe(NO_3)_2$ + $Co(NO_3)_3$	550			
19	$Ni/Fe/SiO_2$ (1/9/90)	$Fe(NO_3)_3$ + $Ni(NO_3)_2$	502			
20	Fe/SiO_2 (1/9)	$Fe(NO_3)_3$	521			
21	Fe/SiO_2 (1/9)	$Fe_2(SO_4)_3$	344			
22	$Na/Fe/SiO_2$ (2/10/90)	$Fe(NO_3)_3$	200			
23	$K/Fe/SiO_2$ (2/10/90)	$Fe(NO_3)_3$	205			
24	Fe/TiO_2 (1/9)	$Fe(NO_3)_3$	11	Commercial, MCB, TX068501, Anatase		
26	$Fe/Activated$ C (1/9)	$Fe(NO_3)_3$	946	Commercial, Union Carbide, LCK, Columbia[R]		
28	$Fe_2O_3 + SiO_2$			Commercial JMC, Puratronic + Fisher SiO_2		
29	$Co/Mo/Al_2O_3$	(Co, 3%; Mo, 9%)		Harshaw Co-Mo-0401		

294